SYNTHESIS AND CHARACTERIZATION OF SILVER FILLED SINGLE-WALL CARBON NANOTUBES

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Abstract. In our study we use simple methodology based on wet chemistry process to fill singlewall carbon nanotubes (SWCNT) with silver nanowires. The novelty of the study comes from very long and continuous silver nanowires being incorporated in the core of single-wall carbon nanotubes with the mean diameter of 1.22 nm. Using high resolution transmission electron microscopy we have clear evidence for the formation of 100-250 nm long silver quantum wires within SWCNT. The structural changes in SWCNT upon filling are discussed using electron diffraction.

1. INTRODUCTION

In order to broaden the potential application of SWCNT they are used as a frame for the growth of new one-dimensional (1D) objects [1-4]. Among many options of altering the properties of carbon nanotubes are partial and complete substitution of carbon atoms coming from SWCNT with heteroatoms like nitrogen and boron, functionalisation of SWCNT with organic molecules bonded non- or covalently to the carbon walls, and filling their hollow interior with the metal. The latter method has extended the potential applications of these materials to possible quantum memory elements, high density magnetic storage media, semiconducting devices, field emitters, scanning probe microscopes [5-10]. Among all metals possible to be filled within carbon nanotubes, silver received the huge attention as the metal with the highest electrical and thermal conductivity. The intercalation of silver within carbon nanotubes can be conducted using capillarity action when melted metals [11,12] or solubilized silver salt are pulled into the cavities of CNTs [13-17].

In this contribution, we apply optimisation of the wet chemistry process in order to produce Ag filled SWCNT. Very high filling ratio with respect to the individual nanotube, as well as to the bulk sample, is obtained with our method. To the best of our knowledge, none of the previous research groups have proved that simple wet chemistry process could be used to produce purified bulk sample of silver filled

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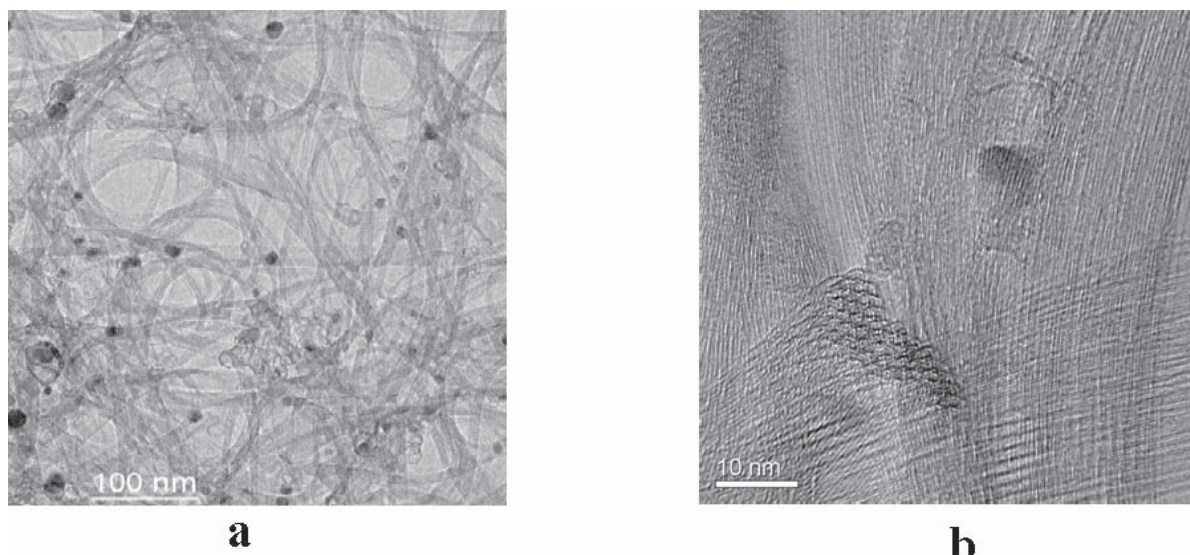Corresponding author: R. J. Kalenczuk, e-mail: rk@ps.pl

Fig. 1. TEM micrographs of as-produced SWCNT (a) and acid treated SWCNT (b).

carbon nanotubes. In our case, silver nanowires are up to several μm long, entire filling the nanotube (mean filling ratio ~ 80% for the individual tube).

2. EXPERIMENTAL

The SWCNT pristine material was produced by standard laser ablation technique [18] with 40% SWCNT yield with a mean diameter of 1.22 nm. The as produced material still contains amorphous carbon and catalyst particles (Ni, Co). Chemical acid treatment was performed in order to purify and open the tubes. The soot was placed in 2M HNO_3 and refluxed for 30 h at about 400K. After filtration and washing with distilled water, the opened and purified nanotubes were transferred to the beaker containing over-saturated solution of silver nitrate ($AgNO_3$) and sonicated for about 15 min. The as-prepared solution was stirred for 48 h at room temperature. Washing out $AgNO_3$, which is not incorporated into the tubes, but remains on the walls or in the space between the bundles, was crucial. This was accomplished by multiple centrifugations with distilled water, after each centrifugation cycle (0.5 h, 4000 rpm) the water was removed and replaced. As the final step, the sample was heated in air at 573K to reduce silver nitrate to silver.

$AgNO_3$ filled SWCNT were sonicated in acetone and thin films were prepared on KBr crystals by dropping solution until the dark grey film is formed. Subsequently, the KBr was dissolved in distilled water and films floated off for microstructural and spectroscopic studies by the TEM grids. Afterwards, the film on the grid was heated at 573K. The morphology and chemical composition of the sample was studied using high resolution transmission electron microscopy (TEM) and its energy dispersive X-ray spectroscopy (EDX) mode. The samples for these investigations were prepared from the previously used films by floating them off the crystals in distilled water, leaving them for several hours to dissolve possible impurities, and recapturing them on the standard microscopy grids. In order to record structural changes of Ag-SWCNT in respect to pristine SWCNT, the film on the grid was transferred into the measurement chamber of a purpose-built 170 keV EELS spectrometer [19]. The energy and momentum resolution was set up to 180 meV and 0.03 $Å^{-1}$ for electron diffraction.

3. RESULTS AND DISCUSSION

3.1. Synthesis

The acid treatment of SWCNT opens their ends; it enables the filling of the cores with foreign elements. TEM micrographes in Fig. 1 shows the morphology of as-produced material (Fig.1a) in comparison to the treated carbon nanotubes (Fig.1b). Acid treatment results in purified and open-ended nanotubes. In this step we significantly reduce the number of catalyst particles (Co/Ni), which is under detection limit as shown in EDX measurement (see below in Fig. 2 – lower panel) as well us elimination of unwanted amorphous species.
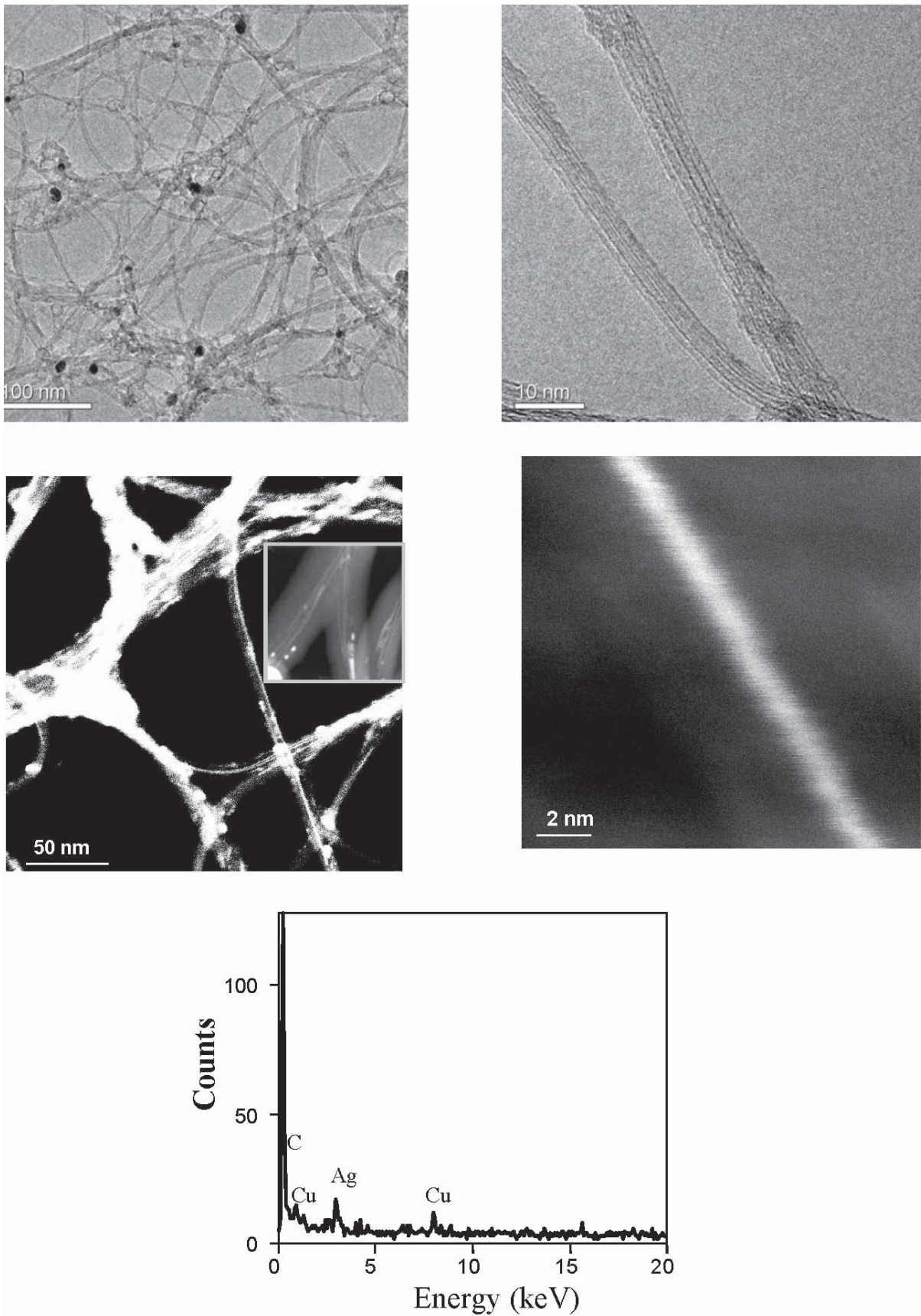
Fig. 2. TEM images of Ag filled SWCNT (upper panel) and dark filled images of the sample (middle panel) with magnifications and EDX spectrum taken from the bundle of filled nanotubes (lower panel).
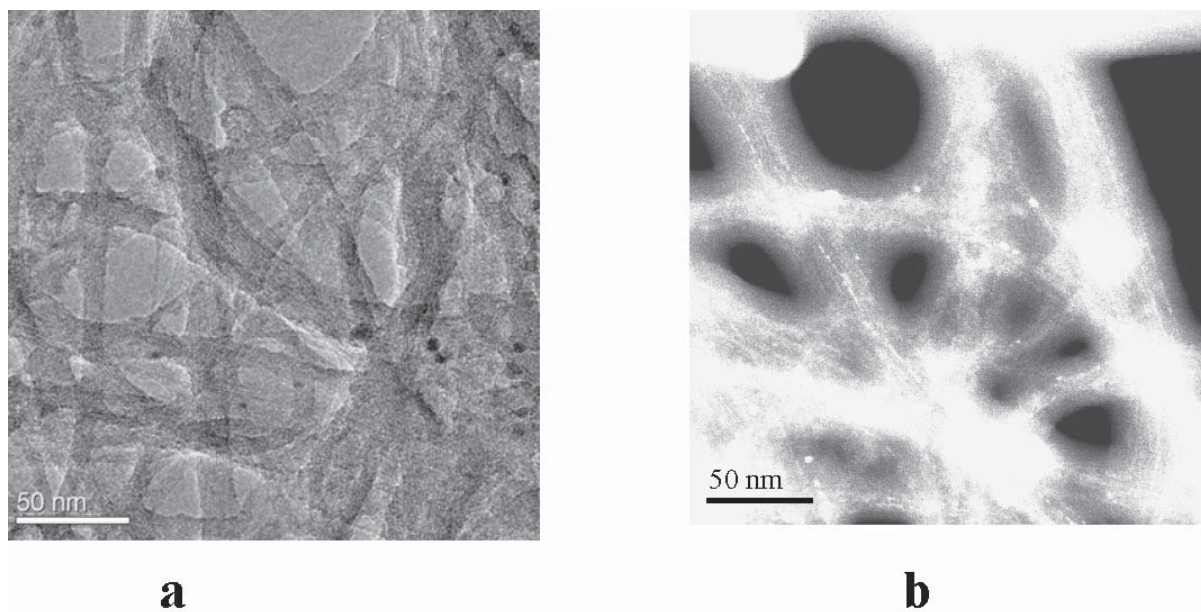
Fig. 3. TEM (a) and HAADF (b) representation of AgNO$_3$ treated SWCNT.

At the next step, AgNO$_3$ in a liquid phase was pulled into the core of SWCNT by capillary action. After filtration, the dark grey sample was collected and dried in air. The liquid phase crystallized in the interiors of the nanotubes efficiently. The thin silver nitrate nanowires encapsulated in SWCNT are presented in bright field TEM image of Fig. 3a, and corresponding dark field TEM image showed in Fig. 3b. The TEM image shows that SWCNT form a composite with AgNO$_3$ being distributed all over the carbon nanotubes bundles. In addition, the high angle dark field images (HAADF) image shows that a large number of the nanotubes is filled. The significant step to obtain pure sample was washing out AgNO$_3$ crystals which were deposited on the surface of the carbon nanotubes and leave the silver nitrate nanowires impregnated in the hollow interiors of the SWCNT. The efficient way to remove the unwanted AgNO$_3$ was multiple centrifugation of the sample in distilled water. Afterwards, the sample was heated at 572K for an hour to reduce the salt to silver.

TEM images resemble the starting SWCNT (Fig. 2 upper panel); however, the dark field dark field images (HAADF) show very thin nanowires with lengths from 20 up to several mm (Fig. 2, middle panel). The detection of the silver filling using standard TEM micrographs was impossible since the diameter of the metal wires was so small that one can not differentiate between individual single nanowires and nanotube walls in the bundle.

The inset of left image in the lower panel of Fig. 2 shows well defined Ag nanowires which exhibit bundle formation with partially Ag filled CNTs, whereas highly filled bundles of SWCNTs were difficult to obtain at the focal plane of the microscope sample.

This effect can be seen in Fig.4, left image of middle panel. EDX spectrum has shown that carbon, silver, and copper (from the TEM grid) are the only elements present in the sample (Fig. 2 lower panel). The high filling ratio with respect to the individual nanotube and large number of filled nanotubes with respect to the starting bulk sample were analysed using high resolution TEM and results in about 80 %.

3.2. Electron diffraction

We carried out a structural analysis using electron diffraction in the EELS spectrometer setting the energy-loss to zero which gave results consistent with X-ray-diffraction analysis [20,21].

The electron diffraction is adequate to investigate the lattice structure and the mean diameter of the bundled SWCNT [22–24], as the intertube distance, including interstitial channels, is mainly dependent on the nanotube diameter. In the diffraction pattern the peaks of SWCNT at lower momentum transfer (up to 2 1/E) are assigned to the diffraction of the bundle formed by SWCNT interacting via van
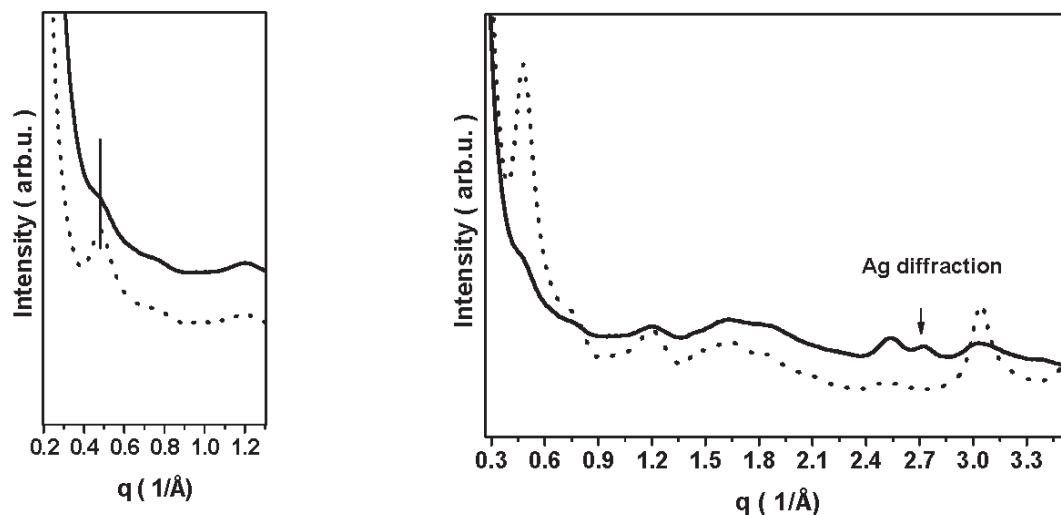
Fig. 4. The first bundle diffraction peak of pristine SWCNT (dotted line) and Ag filled SWCNT (solid line – left panel, and corresponding full range of the bundle diffraction peaks – right panel.

der Waals forces, and that at higher q region are ascribed to in-plane contributions of the graphene layers. One could suspect that upon wet chemistry process, the salt in the liquid phase was able to incorporate in the interior of the SWCNT as well as the interstitial channels between the tubes. The electron diffraction is an easy way to indicate that in the case of Ag filled SWCNT mainly the cores are filled with foreign compound. The left panel of the Fig. 4 represents the first bundle diffraction peak of pristine SWCNT and Ag-SWCNT, respectively. In case of Ag-SWCNT the decrease of the intensity of the peak is observed in respect to pristine SWCNT. This fact provides information that the tubular structure of carbon nanotubes is slightly disorder upon filling and thus a decrease of the respective Bragg peak intensity. The position of the peak remains the same, which indicates that the intertube distance is not changed and mean diameter is the same. Subsequently, it leads to the conclusion that the interstitial channels are free from silver [25]. Additionally, the electron diffraction pattern at higher q (right panel of Fig.4) clearly shows the diffraction peak at ca. 2.78 1/E coming from face-centred cubic (fcc) crystalline silver.

Extremely high metal filling ratio in our work in comparison with other research groups [16-17] can be due to using different starting SWCNT. In our case the mean diameter is 1.22 nm produced by laser ablation while Sloan *et al*. [15] was 1-3 nm,

resulting in ca. 5% yield of filled nanotubes and Z.L. Zhang *et al.* [16] 1-2 nm with ca. 25% of filled nanotubes (both cases arc discharge). In both cases, the yield was estimated based, like in our case, on the electron micrographs observation. The capillarity action depends on the diameter of the tube or container [26]. The height of the liquid is inversely proportional to the tube diameter ($h \sim 1/d$) and according to this simple rule, carbon nanotubes with a mean diameter 1.22 nm have a higher capability to incorporate the liquid than tubes with ranges of 1-2 nm or 1-3 nm as in [15,16]. Thus, the filling is more efficient in our case. Additionally, the opened tubes were reacted with $AgNO_3$ for longer period and clearly improved the yield of filled nanotubes.

To conclude, we have optimised the wet chemistry technique to fill SWCNT with silver. It is very important to point out that the silver nanowires are incorporated into the tubes what was confirmed by the electronic diffraction. In case of 1.22 nm carbon nanotubes and almost two days stirring of the opened nanotubes with silver nitrate have resulted in 80% yield of filled nanotubes in respect to the individual tube.

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